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Synthesis and Electrochemical Properties of Porous $LiAl_{0.05}Mn_{1.95}O_4$ for High Power LIB by Spray Pyrolysis

Takayuki Kodera [a], Syoji Hirose [b] and Takashi Ogihara [b]

Graduate School of Engineering, Materials Science and Engineering, University of Fukui

3-9-1 Bunkyo, Fukui City, Fukui Prefecture 910-8507, Japan

[a] t-kodera@icpc00.ccns.u-fukui.ac.jp, [b] ogihara@matse.u-fukui.ac.jp

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Abstract. Spherical $LiAl_{0.05}Mn_{1.95}O_4$ precursor powders were successfully prepared by spray pyrolysis. $LiAl_{0.05}Mn_{1.95}O_4$ precursor powders were calcined by 800°C for 10hrs. The particles size, morphology, microstructure, crystal phases of the calcined powders were characterized by X-ray diffraction (XRD) and a scanning electron microscope (SEM). The XRD patterns showed that the crystal phases of the calcined powders were the same as spinel phase (space group: Fd3m). The particles exhibited a spherical morphology with a porous microstructure. The particle size of the primary particles was approximately 200nm. $LiAl_{0.05}Mn_{1.95}O_4$ cathodes exhibited higher rechargeable capacity and cycle stability at high rates. The particle microstructure of $LiAl_{0.05}Mn_{1.95}O_4$ powders was effective for the rechargeable capacity at high rates.

Introduction

Lithium ion battery has been widely applied to portable type electronic equipment such as mobile phone, note PC, digital camera because of its high rechargeable capability compared with NiH battery. $LiCoO_2$ [1] has been commercially used as a cathode active material on high energy density lithium ion battery. Recently, lithium ion batteries are well noted as the power sources for the vehicles such as EV and HEV [2]. The lithium ion batteries for EV require cathode materials that combine low cost, high safety and cycle stability at high rates of intercalation / deintercalation. Spinel type $LiMn_2O_4$ is regarded as a promising cathode material for large lithium ion batteries due to their advantages such as low cost, abundance, non-toxicity and thermally stable [3]. It is well known that the doping of Al ion to $LiMn_2O_4$ is most effective for improvement of both thermal and cycle stability [4, 5]. Spray pyrolysis [6] is a versatile process that is used to synthesize oxide and metal fine powders. The advantages of spray pyrolysis are that it allows to control of the particle size, particle size distribution, and particle morphology. In addition, fine powders with a homogeneous composition can be easily synthesized, because the starting solution components are kept in a mist. In this study, spherical $LiAl_{0.05}Mn_{1.95}O_4$ powders with a porous microstructure were prepared by spray pyrolysis. The powder characteristics of them were investigated. The electrochemical properties of $LiAl_{0.05}Mn_{1.95}O_4$ with a porous microstructure were also estimated by rechargeable capacity and cycle performance compared with that of $LiAl_{0.05}Mn_{1.95}O_4$ with a dense microstructure.

Experimental

Spray pyrolysis process [7] was used to prepare $LiAl_{0.05}Mn_{1.95}O_4$ powders. $LiNO_3$, $Al(NO_3)_3 \cdot 9H_2O$ and $Mn(NO_3)_3 \cdot 6H_2O$ was used as starting materials. These compounds were dissolved in water at room temperature. The molar ratio of the metal component (Li : Al : Mn) was set to 1 : 0.05 : 1.95 in the starting solution. The concentration of the solution ranged from 0.1 to 1.5 mol/dm^3. The aqueous metal salts solution was misted using a two-fluid nozzle atomizer at 1 dm^3/hr. Air was used as the carrier gas during the preparation of $LiAl_{0.05}Mn_{1.95}O_4$ powders. The generated mist were carried to an

electric furnace by air carrier gas with a flow rate of 20 dm^3/min and then pyrolyzed from 600 to 900 °C. $LiAl_{0.05}Mn_{1.95}O_4$ precursor powders were continuously collected using the bag filters. Furthermore, the precursor powders were calcined at 800 °C for 10 hrs in electric furnace under an air atmosphere. The heating and cooling rates were 5 °C/min and 4 °C/min, respectively. The thermal behavior of the precursor powders was observed using a thermo gravimetric-differential thermal analysis equipment (TG-DTA, Shimadzu, DTG-60). The crystal phase of the precursor powders and the calcined powders were identified by XRD (Shimadzu, XRD-6100) using CuKα radiation. The chemical composition of the calcined powders was determined by inductively coupled plasma atomic emission spectroscopy (ICPAES, SII NanoTechnology, SPS-7800). The particle size, morphology and microstructure of the calcined powders were determined by using SEM (JEOL, JSM-6390). In the SEM images, 200 particles were randomly sampled to determine the average particle size of the calcined powders. Cathodes were prepared using 80 mass% $LiAl_{0.05}Mn_{1.95}O_4$ powders, 10 mass% acetylene black and 10 mass% fluorine resin. Metal lithium (Honjo chemical) was used as an anode. The celgard (Heist, celgard 2400) was used as a separator. 1mol/dm^3 $LiPF_6$ in ethylene carbonate / 1,2-dimethoxyethane (EC : DEC = 1 : 1, Tomiyama pure chemical) was used as the electrolyte. 2032 coin type cell was built up in globe box under an argon atmosphere. The rechargeable capacity and cycle stability of cathodes were measured with a battery tester (Hosen, BTS2004) at between 3.5V and 4.3V.

Results and discussion

The yield of $LiAl_{0.05}Mn_{1.95}O_4$ precursor powders was approximately 200 g/hr with the collection efficiency of 80%. Fig. 1 shows thermal behavior of $LiAl_{0.05}Mn_{1.95}O_4$ precursor powders obtained from the starting solution of 1.5 mol/dm^3. The weight loss of the precursor powders was a few. Therefore, the thermal decomposition of the mist was carried out uniformly after it was introduced into an electric furnace. The crystal phase and crystallinity of $LiAl_{0.05}Mn_{1.95}O_4$ powders were observed by using the XRD. Fig. 2 shows the XRD patterns of $LiAl_{0.05}Mn_{1.95}O_4$ powders obtained from the starting solution of 1.5 mol/dm^3. From these patterns, it was observed that the diffraction patterns of $LiAl_{0.05}Mn_{1.95}O_4$ powders were good agreement with spinel phase (space group: Fd3m), and other phases such as Mn_2O_3 and Al_2O_3 were not observed. The diffraction patterns of $LiAl_{0.05}Mn_{1.95}O_4$ powders obtained from the starting solution of under 1.0 mol/dm^3 were also good agreement with spinel phase. The crystallinity of $LiAl_{0.05}Mn_{1.95}O_4$ powders was similar to that of $LiMn_2O_4$ powders. Chemical analysis revealed that the metal component (Li : Al : Mn) ratio of the calcined powders was agreement with the starting solution component. This suggested that Al ion were uniformly corporated to lithium manganese oxide by spray pyrolysis. Fig. 3 shows the SEM images of $LiAl_{0.05}Mn_{1.95}O_4$ powders obtained from the starting solution of 1.5 mol/dm^3. When the

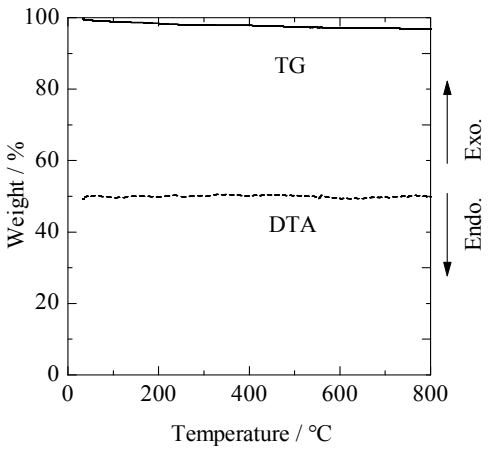

Fig. 1 The thermal behavior of $LiAl_{0.05}Mn_{1.95}O_4$ precursor powders obtained from the starting solution of 1.5 mol/dm^3.

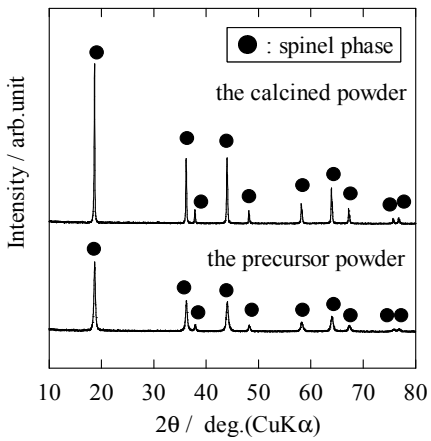

Fig. 2 XRD patterns of $LiAl_{0.05}Mn_{1.95}O_4$ powders obtained from the starting solution of 1.5 mol/dm^3.

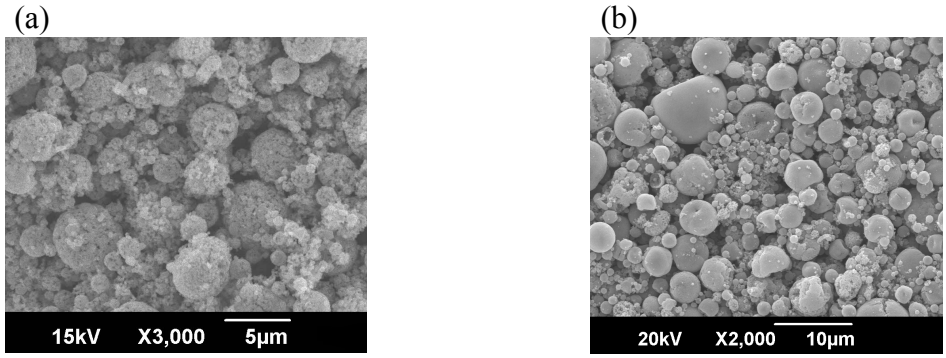

Fig. 3 SEM images of $LiAl_{0.05}Mn_{1.95}O_4$ powders obtained from the starting solution of 1.5mol/dm^3 when changing the pyrolysis temperature. (a) From 720 to 900 °C, (b) From 600 to 750 °C

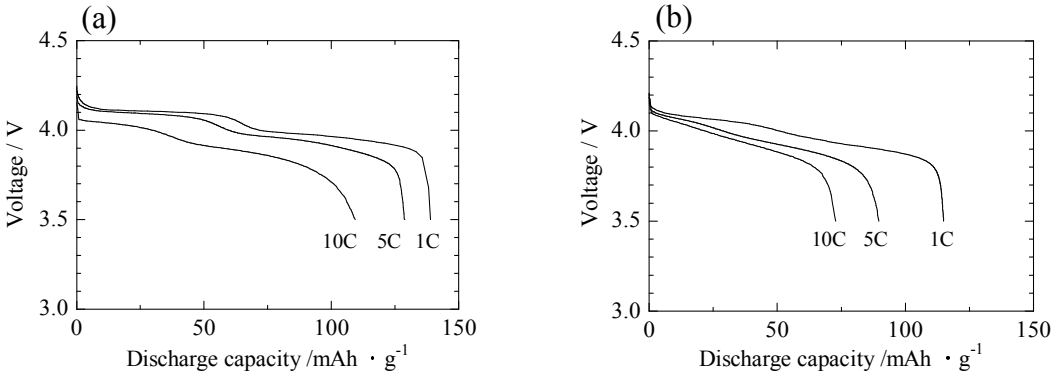

Fig. 4 Discharge curves of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes at 20 °C. (a) $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure, (b) $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure

pyrolysis temperature was from 720 to 900 °C, the particles exhibited a spherical morphology with a porous microstructure. The average size was approximately 2μm. The particle size of the primary particles was approximately 200nm. On the other hand, when the pyrolysis temperature was from 600 to 750 °C, the particles exhibited a spherical morphology with a dense microstructure. When the pyrolysis temperature was from 720 to 900 °C, it was found that the thermal decomposition of the mist was carried out before the drying and the contraction of the mist were completed. Therefore, the sintering of the primary particles was suppressed; this resulted in the formation of a porous microstructure. In addition, when the concentration of the starting solution was under 1.0 mol/dm^3, the particles exhibited a spherical morphology with a hollow microstructure.

Fig. 4 shows the discharge curves of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes at 20 °C. The charge and discharge rate was 1C (1hr), 5C (12min) and 10C (6min). For the comparison, the discharge curves of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure were shown in Fig. 4 (b). The discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure was approximately 139mAh/g at 1C (where the theoretical capacity of $LiMn_2O_4$ is 148 mAh/g.). The discharge capacity decreased to approximately 110mAh/g with increasing up to 10C. On the other hand, the discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure was approximately 115mAh/g at 1C. The discharge capacity decreased to approximately 73mAh/g with increasing up to 10C. It was found that the rate performance of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure was high compared with that of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure. The porous microstructure of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes led to the improvement of the rate performance. Fig. 5 shows the relation between cycle number and discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes at 20 °C. The charge and discharge rate was 1C, 5C and 10C. For the comparison, the cycle and rate performance of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure were shown in Fig.5 (b).The discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure gradually decreased with

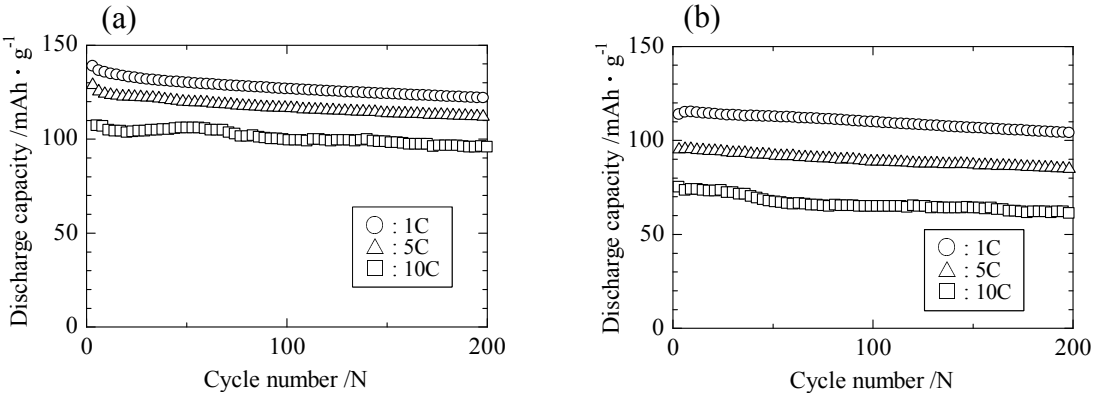

Fig. 5 Cycle and rate performance of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes at 20 °C. (a) $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure, (b) $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure

increasing cycle number. After 200 cycles, 87 % of initial discharge capacity was maintained under the rate of 1 C. On the other hand, 88 % of initial discharge capacity was maintained under the rate of 10 C. It was found that the discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure offered stable cycle performance at high rates. The rate performance of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure was low. However, the cycle performance of that was stable.

Conclusion

Spherical and porous $LiAl_{0.05}Mn_{1.95}O_4$ powders were successfully prepared by spray pyrolysis. XRD revealed that the diffraction peaks of all samples were agreement with spinel phase. The particle microstructure of $LiAl_{0.05}Mn_{1.95}O_4$ powders changed to a porous microstructure by changing the pyrolysis temperature. The rate performance of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure was superior to that of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure. The discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure was approximately 1.5 times that of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a dense microstructure at the rate of 10 C. It was found that the porous microstructure of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes led to the improvement of the rate performance. The electrochemical measurement revealed that the discharge capacity of $LiAl_{0.05}Mn_{1.95}O_4$ cathodes with a porous microstructure had stable cycle performance at high rates.

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